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TITLE: Compositionally Graded Alumina/Mullite Coatings for Protection of Silicon Carbide Ceramic Components from Corrosion

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I. ABSTRACT

OBJECTIVE: The main objective of this research project is the formulation of processes that can be used to prepare compositionally graded alumina/mullite coatings for protection from corrosion of silicon carbide components (monolithic or composite) used or proposed to be used in coal utilization systems (e.g., combustion chamber liners, heat exchanger tubes, particulate removal filters, and turbine components) and other energy-related applications. Mullite will be employed as the inner (base) layer and the composition of the film will be continuously changed to a layer of pure alumina, which will function as the actual protective coating of the component. Chemical vapor deposition reactions of silica, alumina, and aluminosilicates (mullite) through hydrolysis of aluminum and silicon chlorides in the presence of CO_2 and H_2 will be employed to deposit compositionally graded films of mullite and alumina. Our studies will include the kinetic investigation of the silica, alumina, and aluminosilicate deposition processes, characterization of the composition, microstructure, surface morphology, and mechanical behavior of the prepared films, and modelling of the various deposition processes.

WORK DONE AND CONCLUSIONS: A chemical vapor deposition system was developed and constructed for the preparation of metal oxide films from mixtures of metal chlorides, CO_2, and H_2. The developed CVD system includes bubblers for delivery of metal chlorides existing in liquid form at standard conditions and reactors for production of chlorides existing in solid form through chlorination of metals. The system was used to carry out a systematic investigation of the kinetics of the codeposition of silica, alumina, and aluminosilicates from $SiCl_4$, $AlCl_3$, CO_2, and H_2 mixtures. Experiments were also conducted on the codeposition of C and SiC from ethylene and chlorosilane mixtures. Various combinations of feed composition, pressure, and temperature were employed in the oxide deposition experiments, chosen on the basis of the results of the extensive investigation of the thermochemical equilibrium of the Al/Si/Cl/O/H that was carried out in the first year of the project. The results showed that when deposition is carried out from mixtures containing both $SiCl_4$ and $AlCl_3$, the overall deposition rate is much larger (by more than a factor of 2) than the sum of the deposition rates that are observed when only one of the two chlorides is present in the gas phase (along with CO_2 and H_2), at the same concentration as in the mixture. The analysis of the composition of the deposit showed that the increase in the deposition rate is followed by a dramatic enhancement of the deposition of SiO_2 and a reduction in the rate of Al_2O_3 deposition. Preliminary results on profiles of deposition rate and deposit composition in the reactor showed that the content

of the deposit in Al_2O_3 tends to increase towards the entrance of the reactor, reaching for some conditions that corresponding to mullite.

SIGNIFICANCE TO THE FOSSIL ENERGY PROGRAM: Silicon carbide, in monolithic or composite form, exhibits such a unique combination of exceptional high temperature properties that it is ideally suited for use as structural component material in advanced coal technologies, such as IGCC (integrated gasification combined cycle) and PFBC (pressurized fluidized-combustion) systems. However, in the presence of alkali, sulfur, and halide species, SiC exhibits rather poor resistance to oxidation because the SiO2 protective scale that is formed on its surface in an oxidizing environment is destroyed. Successful conclusion of this project will lead to development of methods that can be employed to prepare mechanically and thermally stable coatings for silicon carbide components that will be capable of undergoing a large number of thermal cycles without damage. It will also lead to preparation of protective coating for other materials with very good properties for energy-related applications, such carbon matrix composites.

PLANS FOR THE COMING YEAR: The work on the study of the deposition of silica, alumina, and aluminosilicates from mixtures of metal chlorides, H_2, and CO_2 will be continued. Emphasis will be placed on the elucidation of the origin of the enhancement of the deposition of silica in the presence of AlCl3 in the feed and the identification of ways in which this phenomenon can be suppressed. Chemical vapor deposition experiments will be carried using various combinations of feed composition, pressure, and temperature on refractory wire substrates placed along the centerline of the vertical CVD reactor. The wires will be sectioned at various positions, and the sections will be analyzed using a variety of methods to construct profiles of deposition rate and deposit composition and morphology along the length of the CVD reactor.

II. HIGHLIGHT ACCOMPLISHMENTS

A chemical vapor deposition system was developed for preparation of metal oxide films and used to carry out a systematic investigation of the kinetics of the codeposition of silica, alumina, and aluminosilicates from $SiCl_4$, $AlCl_3$, CO_2, and H_2 mixtures.

The study of the kinetics of the codeposition C and SiC from ethylene and chlorosilane mixtures that was initiated in the first year of the project was completed.

III. ARTICLES AND PRESENTATIONS

Sotirchos, S.V., Kostjuhin, I., Enhanced Deposition of Carbon from Ethylene-Hydrogen Mixtures in the Presence of Chlorosilanes, Proc. of the 14th Int. Conf. on Chem. Vap. Dep., pp. 512-519, The Electrochem. Soc., Pennington, NJ, 1997 (presented at the conference, Paris, September 1997).

Kostjuhin, I., Sotirchos, S.V., Chlorosilane Effects on the Preparation of Functionally Graded SiC/C Materials through CVD from Chlorosilane-Hydrocarbon-Hydrogen Mixtures, 1997 Annual MRS Meeting, Boston, December 1997.

Sotirchos, S.V., Nitodas, S.F., Feasibility of the Preparation of Functionally Graded Alumina-Mullite Coatings through Chemical Vapor Deposition from $AlCl_3$-$SiCl_4$ Mixtures in CO_2-H_2, 1997 Annual AIChE Meeting, Los Angeles, CA, November 1997.

Sotirchos, S.V., Mathematical Modelling of the Densification of Fibrous Structures, to be presented at the 9th Int. Conf. on Modern Materials and Technologies, Florence, Italy, June 1998.

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STUDENTS THAT HAVE BEEN SUPPORTED BY THIS GRANT SINCE ITS INCEPTION:

I. Kostjuhin, Ph.D., S. Nitodas, Ph.D.

PUBLICATIONS AND PRESENTATIONS SINCE THE INCEPTION OF THE GRANT:

Sotirchos, S.V., Kostjuhin, I., Hysteresis Phenomena in the Codeposition of SiC and C from Chlorosilane-Ethylene Mixtures, 1997 ACerS Annual Meeting, Cincinnati, OH, May 1997.

Sotirchos, S.V., Kostjuhin, I., Enhanced Deposition of Carbon from Ethylene-Hydrogen Mixtures in the Presence of Chlorosilanes, Proc. of the 14th Int. Conf. on Chem. Vap. Dep., pp. 512-519, The Electrochem. Soc., Pennington, NJ, 1997 (presented at the conference, Paris, September 1997).

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